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THE EFFECT OF FERROUS COMPOUNDS ON SINTERING OF CLAY MIXTURES UNDER DECREASED PRESSURE OF FIRING MEDIUM

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It is demonstrated that when clays mixtures are fired under decreased pressure, ferrous compounds intensely transform into active forms due to the reducing type of gaseous medium. At the same time the mechanism of modification transformations changes, which contributes to improving the physicomechanical properties of products obtained.

In estimating the significance of the main components of argillaceous rocks, ferrous compounds are usually regarded as colorant elements. At the same time, the study of the effect of iron-bearing compounds on the sintering of argillaceous rocks indicates that depending of the type of the firing medium they have a positive (formation of wustite FeO and its participation in the formation of the vitreous phase) or a negative (formation of “fly” defects, swelling) effect. Due to the diversity of modification transformations, changing stoichiometry, and chemical activity, they have a dual effect on sintering of ceramic mixtures. Undoubtedly, the effect of ferrous compounds on sintering depends on their content in the initial material.

In many regions of our country ceramics are currently produced from low-grade local argillaceous rocks in which the content of ferrous compounds reaches 12%.

Therefore, the study of the behavior of ferrous compounds in clays rocks under thermal treatment and their transformation into active forms for the purpose of intensifying sintering by a controlled modification of the firing medium parameters is of both theoretical and practical interest. This line of research provides a deeper understanding of the mechanism of modification transformations of iron under different thermodynamic conditions and make its possible to identify in more detail their role in the sintering of ceramic

mixtures, as well as develop new techniques for controlling the structure formation and properties of products depending on the quality of raw materials.

In the present study we used a simple technique, i.e., developing a decreased pressure in the firing zone to generate active forms of iron, which, accordingly, decreases the content and partial pressure of oxygen in the gaseous medium. It was earlier established [1] that under such thermodynamic conditions the gaseous medium becomes highly reducing due to the gases being emitted. As a consequence, the gaseous and solid products of thermal reactions react with ferrous compounds and yield their active forms, which play the main role in sintering and formation of the material's structure.

We investigated low-melting Shuiskoe and Shagonarskoe clays from the Republic of Tuva. The prevailing mineral in Shuiskoe clay is illite and the prevailing mineral in Shagonarskoe clay is montmorillonite. Table 1 lists the chemical compositions of the initial clays.

The study was performed according to the following method. Samples of dried and milled clays were used to make cylindrical samples of height 15 mm by dry molding at a pressure of 100 MPa. Thermal treatment was performed in a laboratory electric furnace with platinum heaters in a temperature interval from 100 to 1100°C. The main physiochemical processes with the participation of ferrous compounds take place within these limits. The isothermic exposure at the

TABLE 1

Clay	Mass content, %									
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	calcination loss
Shuiskoe	54.02	16.67	0.97	8.26	3.90	3.21	2.01	0.85	0.14	6.57
Shagonarskoe	55.14	15.82	0.59	9.60	5.01	3.14	1.64	1.09	1.23	8.73

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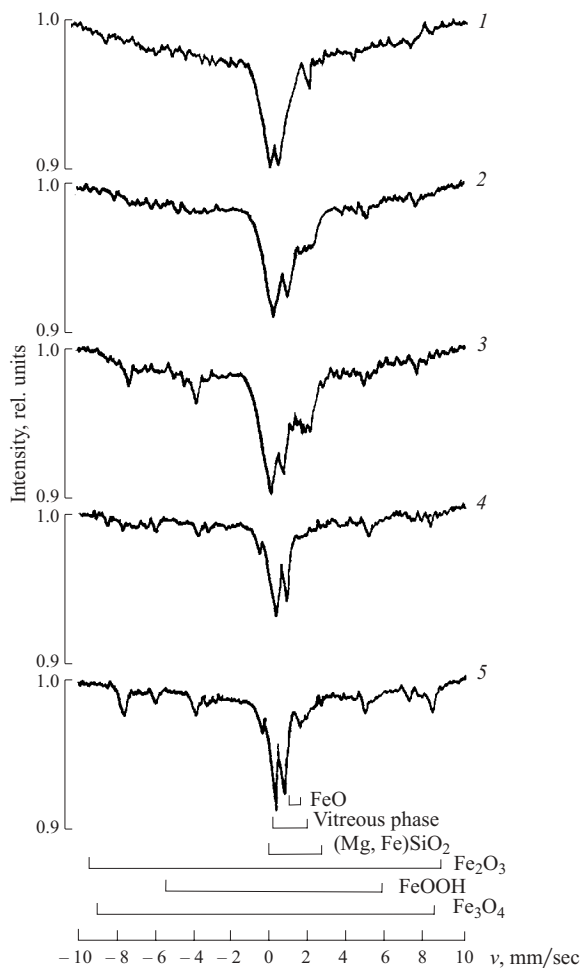


Fig. 1. Mossbauer spectra of Shuiskoe clay samples: 1) initial clay; 2) 900°C under decreased pressure; 3) 1000°C under decreased pressure; 4) 900°C under normal pressure; 5) 1000°C under normal pressure.

final temperature amounted to 1 h. To create a decreased pressure, an electric microfurnace was placed in a special glass vessel from which air was pumped out; as a consequence, the pressure of the firing atmosphere varied from 133×10^3 to 133 Pa.

Iron-bearing minerals in argillaceous rocks and their subsequent phase transformation in firing were identified using Mossbauer spectroscopy (nuclear gamma-resonance spectroscopy, NGRS). The source of Mossbauer gamma-quanta was Co-57 in a palladium matrix. The energy scale was calibrated with respect to metallic iron. The spectra were used to determine the parameters of iron: chemical shift δ , quadrupole splitting ε , and the effective magnetic field H [2]. This method makes it possible not only to obtain complete and reliable information on the form of iron incorporated in argillaceous minerals but also to reveal the number of structural positions and the nature of their distribution. Furthermore, the ratio of bivalent to trivalent iron can be used to estimate

TABLE 2

Clay	Mass content, %	
	Fe ³⁺	Fe ²⁺
Shuiskoe	92	8
Shagonarskoe	90	10

the redox processes occurring in the sintering of ceramic mixtures.

Iron exists in argillaceous rocks in various forms: in free compounds (oxides) and in a fixed state (certain silicates and isomorphic substitutions). Iron hydroxide aggregates of gray brown and reddish hues in low-melting ferrous clays from Tuva have the form of tarnish and films. Nonsilicate iron compounds typically contain weakly crystallized particles with a high degree of dispersion.

Analysis of the spectra (Fig. 1) of Shuiskoe hydromica clay has revealed the presence of goethite α -FeOOH with the parameters $\delta = 1.36$ mm/sec, $\varepsilon = 1.97$ mm/sec and another iron hydroxide with trivalent iron and the parameters $\delta = 0.35$ mm/sec, $\varepsilon = 0.53$ mm/sec. Along with the specified ferrous compounds, the Shuiskoe clay spectrum has a third low-intensity doublet related to iron ions contained in silicates. It should be noted that similar Mossbauer spectra were earlier observed in the analysis of clays containing iron-magnesian mica and chlorite [3].

Shagonarskoe montmorillonite clay along with goethite contains hematite with the parameters $\delta = 0.54$ mm/sec and $\varepsilon = 0.19$ mm/sec. The decreased value of the magnetic field of hematite (497 kOe) may be attributed to a high degree of dispersion of particles. Besides, there exist spectra consisting of incompletely resolved doublets corresponding to Fe²⁺ ions. Such spectra are typical of the ferromagnetic phase, i.e., siderite FeCO₃.

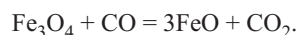
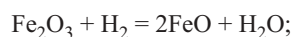
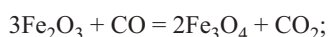
The processing of obtained NGRS spectra using a specialized program made it possible to determine the relative share of heterovalent iron ions in argillaceous clays. Ferrous compounds in the initial clays exist mainly in the trivalent state and the share of Fe²⁺ is insignificant (Table 2). Based on the ratio between bi- and trivalent iron, which is an important index of the redox potential, Tuva clays are nearly no different from known argillaceous rocks [4].

After the start of heat treatment at a pressure of 133×10^3 Pa and temperature of 320°C, a new component emerges in the Shuiskoe clay spectra with the parameters $\delta = 0.31$ mm/sec, $\varepsilon = 0.26$ mm/sec, and $H = 512$ kOe typical of α -Fe₂O₃. The wide peaks of the spectrum gradually become narrower with increasing temperature, which points to a high degree of crystallization of the phase. The transition dynamics is as follows: up to 700°C the content of hematite reaches 30% and at temperatures of 800, 900, 1000, and 1100°C it reaches 40, 55, 75, and 95%, respectively. It was found that even at a temperature of 1100°C iron hydroxides are registered in the inner layers of the material.

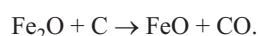
The spectra of samples fired at a temperature of 500°C starts exhibiting the lines of magnetite Fe_3O_4 . At a temperature over 700°C a third doublet is registered with parameters $\delta = 0.99$ mm/sec and $\varepsilon = 1.77$ mm/sec corresponding to bivalent iron. The relative intensity of magnetite and wustite doublets is insignificant. At 1100°C the content of bivalent iron is not more than 18% of the total iron content (Table 3).

The thermal treatment of Shuiskoe clay under decreased pressure (133 – 399 Pa) significantly modifies the mechanism of modification transformations. While a decreased partial pressure of the gaseous medium does not affect the beginning of hematite formation (300°C), doublets with the parameters $\delta = 0.36$ mm/sec, $\varepsilon = 0.15$ mm/sec, and $H = 483$ kOe typical of magnetite emerge in the spectra starting with a temperature of 360°C. This early formation of magnetite corroborates its instability under changing parameters of the firing medium. At the same time, doublets corresponding to bivalent iron were identified simultaneously with the magnetite doublet. It should be noted that Fe^{2+} is present not only in wustite, but in silicates as well.

With increasing temperature the content of bivalent iron, especially of wustite, gradually increases. This is primarily due to the changing gaseous medium inside the material. Earlier [5] mass-spectroscopic analysis established that under decreased pressure the gaseous atmosphere in clay firing (300 – 1000°C) always remains reducing due to the gases released from ceramics. The content of reducing gases (H_2 , CO) in the gaseous atmosphere during the entire firing of Shuiskoe and Shagonarskoe clays varies from 29 to 57 vol.%. The high content of reducing gases CO and H_2 , which are the products of burning of organic compounds, facilitates the following reactions with the participation of ferrous compounds:



The reduction of wustite within the temperature interval of 400 – 700°C is also due to carbon accumulated in the inner layers of the material after the oxidation and burning of organic compounds (the content of organic materials in Shuiskoe and Shagonarskoe clay is 0.86 and 0.67% converted to dry carbon):



The sequence of phase transformation of ferrous compounds agrees well with the results of gas analysis and NGRS. The reduction of magnetite and wustite taking into account the products of decomposition of carbonates (CO and H_2) is corroborated by a gradual increase in the content of carbon dioxide (up to 52%) in the gaseous atmosphere at 700 – 1000°C. The quantitative ratio of bivalent iron to total

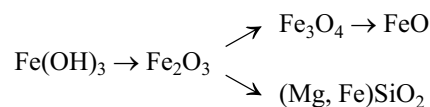
TABLE 3

Firing temperature, °C	$\text{Fe}^{2+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio	
	under decreased pressure*	under normal pressure
400	0.14	0.09
500	0.19	0.09
600	0.32	0.10
700	0.48	0.11
800	0.59	0.12
900	0.77	0.14
1000	0.82	0.16
1100	Was not determined	0.17

* 133 – 399 Pa.

iron under decreased pressure at 1000°C grows to 0.82%, i.e., over 80% of the ferrous compounds consist of Fe^{2+} (Table 3). Bivalent iron ions exist mainly in the inner layers of material, since the outward layers are oxidized as the pressure grows to the atmospheric level. An intense transition of ferrous compounds into more active forms due to decreased pressure and a highly reducing medium occurs in the temperature interval of 500 – 900°C. In the range of high temperature (800 – 950°C) the predominant role in the reduction of wustite is played by the coke residue. It was earlier established [5] that a significant decrease in the carbon content in ceramics is observed under decreased pressure within the specified temperature interval.

As a result of the simultaneous effect of decreased pressure and the reducing gaseous atmosphere, the phase composition of Shuiskoe clay fired at 1000°C contains several ferrous compounds. The Mossbauer spectra indicate the presence of hematite, magnetite, wustite, ferrous olivine, and the vitreous phase. The specific feature of Shuiskoe clay sintering under a decreased pressure is the formation of ferrous olivine and the vitreous phase. The emergence of olivine in the spectra having a doublet whose parameters, according to published data [6], are identified as $(\text{Mg}, \text{Fe})\text{SiO}_2$ is due to the dissociation of laminar silicates. Consequently, the behavior of ferrous compounds in thermal treatment under decreased pressure can be described as follows:



Wustite actively participates in the formation of the vitreous phase at temperatures of 650 – 1000°C: Of all iron compounds wustite has the highest reaction capacity. It is mentioned in [7] that the vitreous phase formed on the basis of iron silicates and wustite is more active than the feldspar vitreous phase and has an enhanced dissolving capacity.

It should be noted that ferrous vitreous phases with an enhanced dissolving capacity dissolve quartz particles well and convert them into the vitreous phase. Accordingly, as the content of the ferrous vitreous phase grows due to dissolving

TABLE 4

Firing temperature, °C	Decreased pressure				Normal pressure			
	average density, g/cm ³	volume shrinkage, %	water absorption, %	compressive strength, MPa	average density, g/cm ³	volume shrinkage, %	water absorption, %	compressive strength, MPa
700	1.94	3.7	14.9	35.1	1.91	1.9	17.5	28.4
800	1.97	5.4	11.8	42.3	1.95	4.0	14.4	36.3
900	2.04	9.7	8.7	58.4	1.98	5.8	12.1	44.9
1000	2.13	12.1	5.8	79.8	2.06	10.1	8.3	59.7
1100	Deformation				2.14	12.9	5.2	80.6

free quartz, the mechanical strength of samples fired under a decreased pressure increases.

Analysis of the physicomachanical properties of heat-treated samples of Shuiskoe clay (Table 4) shows that under decreased pressure the sintering process starts earlier (by 100°C) compared to the standard procedure. The degree of sintering can be inferred from the volume shrinkage. Samples fired at a temperature of 900°C under decreased pressure have a volume shrinkage of 9.7% and strength of 58.4 MPa. Approximately the same volume shrinkage and strength is observed in samples fired at 1000°C under normal pressure. A similar regularity is seen in samples based on Shagonarskoe montmorillonite clay as well.

As the firing medium parameters are modified (decreasing pressure and a reducing atmosphere), the shrinkage phenomena become more intense and, accordingly, the water absorption decreases and the strength of samples grows. Shrinkage in ceramics depends on the composition and the physicochemical properties of the liquid vitreous phase. Thus, more viscous vitreous phases with increased moistening capacity are formed on the basis of wustite and other iron silicates. An increased content of the ferrous vitreous phase has a significant effect on the formation of the ceramic structure. Microscopic analysis of Shuiskoe clay indicates that the structural elements of this material fired under normal pressure (at 1000°C) are irregular grains, and the particles are separated by numerous large slot-shaped pores of diameter over 10 µm. At the same time, the content of sealed porosity is insignificant. The structural characteristics of samples fired under a decreased pressure have significant morphological differences. Higher-melting particles are bound by a dark-brown vitreous phase. The contact zones are rounded, which indicates the presence of a viscous glass phase at these sites. Between relatively dense sintered particles one can see fine and large sealed pores of diameter 2 – 5 µm. Most pores are isolated and, consequently, the content of the sealed pores is higher.

The joint effect of decreased pressure and a reducing gaseous medium under firing changes the mechanism of modification transformations of ferrous compounds and their effect on sintering of clay mixtures. First, a decreased partial pressure of the gaseous medium shifts the start of the reactions with the participation of ferrous compounds towards lower temperatures. Second, the reducing type of the gas me-

dium facilitates the transition of ferrous compounds to more reactive forms. Third, the latter participate in the formation of a ferrous glass phase with an enhanced dissolving capacity, which ensures a closer contact between the solid particles.

X-ray analysis identified another iron-bearing phase, namely fayalite $2\text{FeO} \cdot \text{SiO}_2$, in Shagonarskoe clay samples fired at 1000°C under decreased pressure.

To verify the data obtained, household and fancy ceramic products were produced from Shuiskoe clay and fired in a vacuum electric furnace. The firing of experimental samples under decreased pressure (133 – 399 Pa) at a temperature of 920°C yielded glazed majolica products with water absorption of 11.2% and hear resistance over 15 cycles. When fired under normal pressure at the same firing temperature, the products had water absorption 15.1% and were water-permeable and less heat-resistant. Majolica products with water absorption of 11% produced under normal pressure at a temperature of 1000°C showed signs of deformation. Firing majolica products under decreased pressure significantly expands the sintering interval of ceramic mixtures and substantially shortens the firing duration.

Thus, when using argillaceous rocks with a high content of ferrous compounds, in order to accelerate sintering and achieve the required structure of materials it is necessary to decrease the pressure and ensure a reducing type of firing atmosphere.

REFERENCES

1. B. K. Kara-sal, "The effect of gaseous medium on sintering of ceramics mixtures under decreased pressure," *Izv. Vuzov, Ser. Stroito-vo*, Nos. 2 – 3, 44 – 47 (2000).
2. G. S. Wertheim, *The Mossbauer Effect* [Russian translation], Mir, Moscow (1976).
3. S. P. Ekimov, "Characteristics of iron-bearing phases in Cambrian clay," *Neorg. Mater.*, **24**(8), 1353 – 1357 (1988).
4. V. M. Loginov and N. S. Yugai, "Tinting of clay from Gzhel deposit," *Steklo Keram.*, No. 2, 13 – 18 (2000).
5. B. K. Kara-sal, "The effect of decreased pressure on gas emission in clay firing," *Steklo Keram.*, No. 9, 18 – 20 (2004).
6. S. E. Waever, "Mossbauer analysis of iron in clay minerals," *Science*, **156**, 104 – 124 (1977).
7. V. F. Pavlov and I. V. Meshcheryakova, "The effect of iron-bearing low-melting clay additives on modification of the phase composition of acid-resistant materials," in: *Publ. of NIIsroikera-mika Institute* [in Russian], Moscow (1981), pp. 109 – 115.